

### 2.1.6. FLASK MEASUREMENTS OF CARBON MONOXIDE

Carbon monoxide mixing ratios were measured in a subset of flasks collected as part of the cooperative flask sampling program. Measurements were made when glass flasks fitted with Teflon O-ring stopcocks were used to collect the air sample. Table 2.5 lists the land-based sites where CO was measured in 1993, the date of the first CO measurement, and where possible, the 1993 annual mean value for the site. Samples for CO were also collected on trans-Pacific and South China Sea cruises through June 1993 (data not presented). In early 1994 these programs resumed (see section 2.1.2). Analysis of air from flasks for CO and H<sub>2</sub> were made on a semi-automated Trace Analytical RGA. Methane, CO, and H<sub>2</sub> analyses used a common reference gas (AAL-17270, 112.9 ppb CO). The response characteristics of the instrument used for flask analyses were non-linear over the range of atmospheric values. Preliminary CO mixing ratios were calculated using AAL-17270 as an internal reference, final values were determined using a 6-8 point calibration curve [as described in *Peterson and Rosson*, 1993; *Novelli et al.*, 1994a]. The precision of the CO method, estimated as the difference of mixing ratios determined for each flask in a simultaneously collected pair of flasks, was typically 2 ppb or better. An automated flagging routine was installed with flagged flask pairs having a difference of greater than 3 ppb. Hydrogen was referenced to an arbitrary scale awaiting the preparation of accurate standards.

Annual mean CO values for 1993 were calculated for stations that had samples collected during the whole the year (Table 2.5). These mean values were calculated from a curve fit to the complete time series, the smoothed curve reduces the effects of any particular sample on the whole data set. The data are smoothed in time using algorithms developed at CMDL [*Thoning et al.*, 1989].

Mixing ratios of CO determined in flask samples were used to determine the distribution of CO from June 1990 to June 1993. Locations were used that had at least 2 years of measurements before June 30, 1993.

This included 10 fixed sites and 17 shipboard sites from the *Wellington Star* (a similar shipboard sampling program aboard the *Southland Star* is described by *Lang et al.* [1992]). Each of these 27 sites showed a decrease in CO over the 3-yr period. The data from each site was smoothed in time as described previously, and a meridional curve was fit to each biweekly period. These curves represent the surface presented in Figure 2.15.

These smoothed data were combined to calculate a quasi-global average CO mixing ratio (inset, Figure 2.15). There was a slow decrease in CO levels during 1990 and 1991, then CO levels dropped sharply in 1992 and the first half of 1993. Possible reasons for this change include decreases in CO emissions because of decreases in fossil fuel combustion and biomass burning, or an increase in CO oxidation from increased levels of OH [*Bakwin et al.*, 1994; *Novelli et al.*, 1994b].

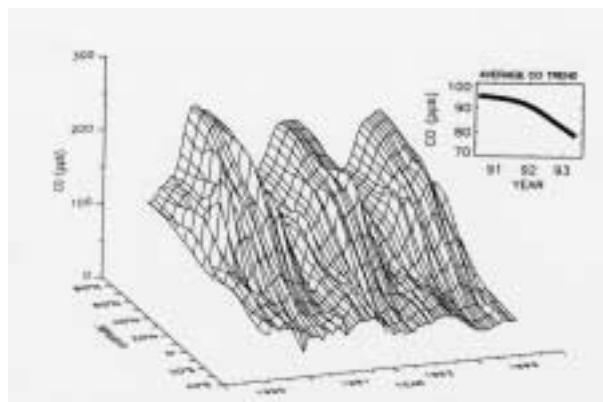


Fig. 2.15. Three-dimensional representation of the distribution of CO in the marine boundary layer. The surface represents data smoothed in time and latitude for the period June 1, 1990, to June 30, 1993. The inset shows the average CO mixing ratio during this period.